

INVITED TOPICAL REVIEW

POLYMER COMBUSTION AND FLAMMABILITY—ROLE OF THE CONDENSED PHASE*

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The combustion process of polymers is a complex coupling of energy feedback from a flame to the polymer surface with gasification of the polymer to generate combustible degradation products. Although there are extensive studies of the effects of wind velocity, gas phase oxygen concentration, external thermal radiation, and gravity on the combustion of polymers, the effects of polymer characteristics on combustion and flammability are not nearly as well understood as those in the gas phase. At present, detailed governing equations for continuity, momentum, energy, and chemical species concentration in the gas phase can readily be written with appropriate boundary conditions, and their solutions can be derived for various cases. However, even those governing equations cannot be derived for the condensed phase without understanding of the governing chemical and physical processes that control the gasification of polymers. This paper concentrates on describing various observed phenomena in polymers (which have been often ignored or neglected) during their combustion, some or all of which might have significant effects on the burning rate and flammability properties. Because of a lack of understanding of the basic combustion mechanisms of polymers, theoretical models able to predict combustion phenomena and flammability properties are not available. In order to overcome this problem, global material characteristics are currently measured by well-defined test methods, and the results are used as inputs to fire growth models intended to predict behavior of the materials in specific fire scenarios. To improve the fire performance of polymers, a nonhalogenated char-forming flame-retardant approach is suggested, and its benefits are discussed.

Introduction

Synthetic polymers are a pervasive part of today's society. They can be found in nearly every commercial building, residential house, transportation vehicle, etc.; they permeate our surroundings. Total polymer production in the USA in 1992 was roughly 26 million tons [1] (additional 5 million tons for synthetic rubber and fibers), and it is expected that a similar amount of polymer production will continue. Today, synthetic polymer materials are rapidly replacing more traditional materials such as steel and nonferrous metals and natural polymeric materials such as wood, cotton, natural rubber, and so on, but they also are original materials in their own right, possessing uniquely valuable physical properties. However, one weak aspect of synthetic polymer materials compared with steel and other metals is that these materials are combustible under certain conditions. Thus, the majority of polymer-containing end products (for example, cables, carpets, furniture) must pass some type of regulatory test to help assure public safety from fire. Therefore, it is important to

understand how synthetic polymers burn and how to modify the materials to make them less flammable in order to pass such tests without compromising the uniquely valuable physical properties. This paper describes the current understanding of the role of the condensed phase in combustion of synthetic polymers, theoretical modeling in the condensed phase, flammability measurement, and methods to reduce their flammability.

Combustion Process

Combustion of synthetic polymer materials is characterized by a complex coupling between condensed and gas phase phenomena. Furthermore, the phenomena in each phase consist of a complex coupling of chemical reactions with heat and mass transfer processes, as described later. Since the gas phase phenomena, such as chemical reaction, turbulence, soot formation, and so on, have been extensively studied and described elsewhere, this paper concentrates on the less-explored condensed phase phenomena and their role in flammability.

Radiative Heat Transfer:

In order to burn a polymeric material, thermal energy must be added to the material to raise its tem-

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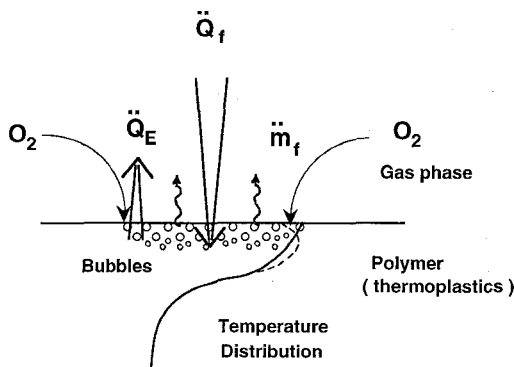


FIG. 1. Schematic illustration of polymer (thermoplastic) gasification. The solid line is the temperature distribution for an opaque material, and the dashed line is for a diathermic material.

perature sufficiently to initiate degradation. This energy could be from an external source, in the case of an ignition event, or from an adjacent flame as energy feedback in the case of flame spread and burning. Thermal radiation is a primary mode of energy transfer from the flame to the polymer surface except for small samples (roughly less than 10-cm diameter) [2-6]. The amount of energy absorbed by the polymeric material depends on the level and the spectral characteristic of the radiant flux, absorption characteristics of the material, and the material surface reflectance with respect to the emission spectrum of the incident radiation [7-10]. Generally, the emission spectra of large flames are continuous in the infrared, as a result of high-temperature soot particles, with additional strong emission bands from H_2O and CO_2 [6]. The absorption spectra of polymeric materials consist of numerous absorption bands in the infrared wavelength region, depending on the vibration modes of the molecular bonds in the polymer structure [11,12]. If the effective absorption coefficient of the material with respect to the external radiation is small, a large amount of the material beneath the surface is heated, which slows the rate at which the material approaches its degradation temperature range. However, if the effective absorption coefficient is large, most of the radiation is absorbed close to the surface, and a thin layer of the material is rapidly heated to its degradation temperature range. In this case, the ignition delay time becomes shorter for the same external radiant flux [13,14]. Also, the maximum temperature in the material is at the surface with an opaque material instead of below the surface with in-depth absorption [9,10,13]. Two different temperature distributions are shown in Fig. 1. The solid line is the temperature distribution for an opaque material, and the dashed line is for a diathermic material. As described below, bubbles are often formed at/near the surface of a thermoplastic

sample.** There are no published papers concerning how significantly the bubbles affect the heat transfer process in the sample by modifying heat conduction and/or scattering the incident external radiation, but potential effects could be large.

Degradation Reactions:

When temperatures near the surface become high, thermal degradation reactions occur and evolve small gaseous degradation products. The majority of the evolved products is combustible. Depending on the nature of the polymer, thermal degradation reactions may proceed by various paths. Since there are several recent books and articles describing thermal degradation chemistry in detail [15-17], only an extremely brief discussion is presented here. It has been accepted that the majority of vinyl polymers degrade thermally by a free radical chain reaction path. Free radical chain reactions consist of random or chain-end-initiated scission, depropagation, intermolecular or intramolecular transfer, and termination reactions. Polyethylene (PE) is a typical example of a polymer that undergoes scission at random locations on the main chain to yield many smaller molecular fragments. Polystyrene (PS), polypropylene (PP), and polymethylacrylate (PMA) belong to this group. Polymethylmethacrylate (PMMA) undergoes a reversal of the polymerization reaction after the initial breakage and yields mainly monomer molecules. Polyoxymethylene, poly- α -methylstyrene, and polytetrafluoroethylene belong to this group. These two groups of polymers undergo almost complete degradation while leaving hardly any char (carbonized polymer residue). Polymers with reactive side groups attached to the backbone of a polymer chain may first degrade as a result of interactions or instabilities of these groups; such reactions may then lead to scission of the backbone. Polyvinylchloride (PVC) and polyvinyl alcohol (PVA) are examples of such polymers. This group tends to undergo cyclization, condensation, recombination, or other reactions that ultimately yield some char. Diene polymers, polyacrylonitrile, and many aromatic and heterocyclic backbone polymers also belong to this char-forming group. Common to the pyrolysis of all these polymers is the formation of conjugated multiple bonds, transition from a linear to a cross-linked structure, and an increase of the aromaticity of the polymer residue [18]. For polymers containing aromatic carbon and/or heterocyclic links in the main chain of the polymer structure, general features of their pyrolysis and char

**Most linear or branched polymers can be made to soften and take on new shapes by the application of heat and pressure. These polymers are said to be thermoplastic. The cross-linked polymers (with cross-linkages among different polymer chains) cannot be made to soften and/or melt.

yield have been derived [19,20]. Some features are as follows: (1) the thermal stability and the char yield increase with the relative number of aromatic groups in the main chain per repeat unit of the polymer chain; (2) the thermal stability of heterocyclic polymers increases with the aromatic component of the heterocycles; and (3) pyrolysis begins with the scission of the weakest bonds in the bridging groups connecting the aromatic rings or heterocycles. Char-forming thermoplastics often swell and intumesce during their degradation/combustion, and one recent flame-retardant approach is to promote the formation of such intumescent char, as discussed later in this paper.

Degradation of a polymer is often affected by the presence of abnormal structures that are usually less thermally stable than the regular structures. Some such structures are inherent consequences of the method of polymerization. If a vinyl polymer is polymerized with a free radical initiator, termination reactions yield unsaturated end groups and also a head-to-head linkage within the chain. These abnormal structures were found in PMMA, and it was shown that they lowered the thermal stability of the polymer and reduced ignition delay time and increased burning rate [21,22].

Mass Transport:

As described above, the type of polymer structure, thermal properties, and the amount of heat transferred to the polymer determine the depth over which the polymer is heated sufficiently to degrade. Since the boiling temperatures of some of the degradation products are much less than the polymer degradation temperatures, these products are superheated as they form. They nucleate and form bubbles. Then, these bubbles grow with the supply of more small degradation products to the bubbles by diffusion from the surrounding molten polymer [23]. Since the polymer temperature is higher near the surface than further below, the polymer sample is more degraded there, and its molecular weight, M , is lower. Since the viscosity of the molten polymer, η , depends strongly on molecular weight and temperature (for example, $\eta = cM^{3.4}$ or $\eta = \exp\{-M/(E(T - T_g))\}$ [24]), the viscosity near the surface is much less than that in the interior. The net result is a highly complex generation and transport of bubbles containing small molecules from the interior of the polymer melt outward through a strong viscosity gradient that heavily influences bubble behavior. A qualitative description of this complex transport process and its effect on gasification rate has been given in Ref. 25. These complex effects of the temperature distribution in PMMA and the bubble formation at the time of piloted ignition are clearly seen in Fig. 2 [26].

To avoid the complex coupling between the gas

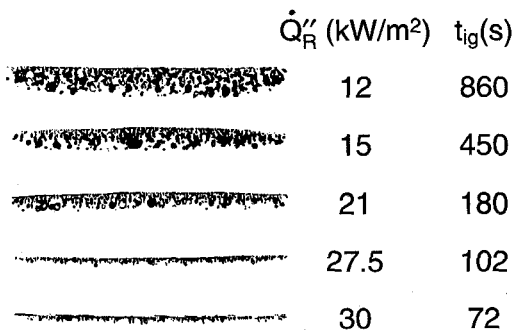


FIG. 2. Cross sections through samples of acrylic sheet that had been ignited at different external radiant fluxes but immediately quenched (Ref. 26).

phase and the condensed phase and also to avoid a configuration-dependent energy feedback rate (horizontal vs vertical configuration; also sample size effects), another approach, using a well-controlled external thermal radiation flux simulating the energy feedback from a flame, has been used to study the polymer gasification process [27–33]. Advantages of this approach over a burning polymer configuration are as follows: (1) heat flux can be independently changed, and (2) the surrounding gas composition can be also independently changed. Vovelle et al. [34] and Kashiwagi and Ohlemiller [25] studied the gasification rate of PMMA. They observed an increase in the transient gasification rate after surface temperature reached a constant value and concluded that degradation in the subsurface region of the sample contributes to the rate of gasification. Although it has been assumed that the degradation products generated in the subsurface region are instantaneously transported to the sample surface [34], the transport might become a rate-controlling step particularly at high temperatures [25] and at high heating rates [35]. As discussed above, polymer melt viscosity could have significant effects on bubble transport through a thermoplastic. The effects of initial molecular weight of PS (about a factor of 2) on gasification rate were studied at external radiant fluxes of 1.7 and 3.9 W/cm². However, here it was found that the effects were not significant, probably because of a rapid reduction in molecular weight by chain scissions, which would reduce the difference in molecular weight between the two samples used [22]. At present, it is clear that the subsurface degradation is important for the gasification, but it is not clear what the main transport process for the small degradation products to the sample surface is and also how rapid this transport is. It appears that diffusion of small molecule gases through a polymer is too slow to be responsible for the transport of the products [36].

Oxidative Degradation:

Not only pyrolysis reactions but also oxidative degradations in the condensed phase might significantly affect the gasification rate of a polymer if enough gas phase oxygen is transported to the polymer surface during combustion of the polymer. In order to determine the effects of oxidative degradation on the gasification process, further studies of radiative heating behavior have included measurements of the molecular weight distribution [28,37] and temperature distribution in the sample [34], the oxygen concentration in the sample by elemental analysis [28], bubble sizes (qualitatively) [25], and evolved gas analyses [28]. Brauman [38] concluded that surrounding oxygen does not affect the polymer degradation process in steady-state burning or in steady-state radiative gasification of PS and PMMA. In contrast, in the burning of small-diameter rods of PP, they inferred that condensed phase oxidation occurs, and they suggested that the polymer degrades by oxygen-promoted pyrolysis [28,38]. Stuetz et al. [39] concluded that thermal oxidative reactions at and near the PP surface are the main energy source for the burning process instead of energy feedback rate from the gaseous flame. Their conclusion was based on the measured oxygen concentration (about 26% at the surface) in the quenched sample obtained using neutron activation analysis. However, since oxygen cannot be activated by neutrons, the validity of their measurement is highly questionable. Significant importance of condensed phase oxidation was also found for steady-burning small-diameter rods of PE and PMMA [40] and also for a PE opposed diffusion flame [41]. The latter study estimated that surface oxidation at most accounted for 20% of the energy required for pyrolysis, with the remainder of the energy being delivered to the surface from the flame. These studies measured various gas phase species concentration distributions above the fuel surface, including CO and H₂O, and the importance of the condensed phase oxidation was determined from the gradients of the oxidized species at the sample surface. However, some caution is needed regarding the quantitative accuracy of the gradients, as pointed out by the comments at the end of Ref. 41. These results indicate that oxidative degradation can be of some importance when the gasification rate is relatively low and the evolving gaseous degradation products do not strongly block diffusion of surrounding oxygen into the degrading surface [25]. Such a case is shown in Fig. 3 at an external flux of 1.7 W/cm². When the gasification rate becomes high [25] or the heating rate is high [42], oxidation reactions appear to be less important or insignificant; this trend is shown in Fig. 3 at 4 W/cm². Still, further careful studies are needed to clarify the potential role of oxidative degradation because the competition between pyrolysis and oxidative degradation depends on attendant oxygen

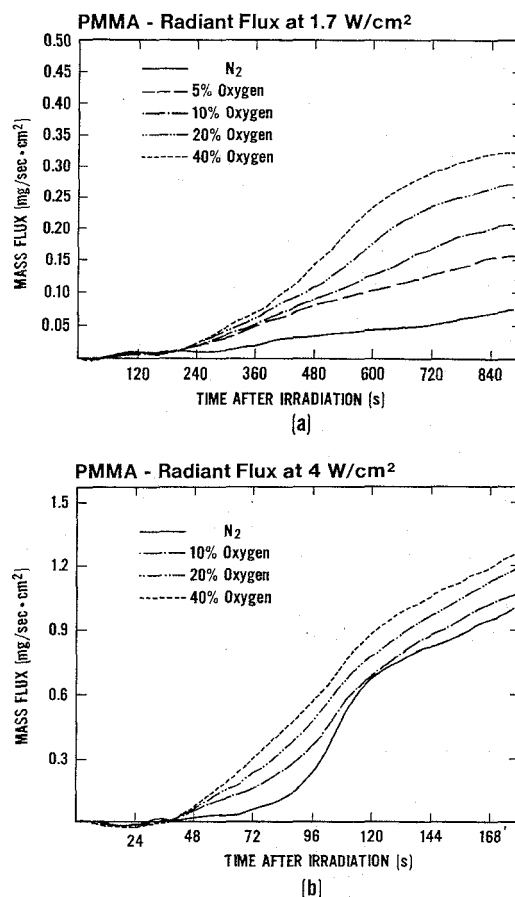


FIG. 3. Histories of mass flux from PMMA (Rohm & Haas Plexiglas G 15-mm thick) after the start of irradiation with various oxygen concentrations in the gas phase: (a) 1.7 W/cm², and (b) 4 W/cm² (Ref. 25).

transport, which is affected by the sample orientation and size, and also on the surrounding flow condition; the range of possibilities has been only lightly explored. The contribution of oxidative degradation could be important for ignition processes at low fluxes (low heating rate) as a result of the fact that it increases the gasification rate. Since the surface heating rate of a PMMA sample during surface flame spread is of the order of 5 °C–10 °C/s [43,44], it appears that the effects of oxidative degradation of the PMMA would be negligible under such high heating rates [42]. However, this does not necessarily mean that the contribution of oxidative degradation to flame spread is always negligible. There is some evidence to demonstrate the participation of oxidative degradation in the flame spread process; this includes detection of peroxide and carbonyl moieties on the surface of PP beneath a horizontally traveling flame front [45]. Further studies with PP and other poly-

mers are needed to determine the extent of the effects of oxidative degradation on flame spread.

Theoretical Models:

Theoretical models describing the above-discussed coupling between the condensed phase and the gas phase are rather limited, although some parts of the processes have been modeled in detail. The details of the thermal degradation of relatively simple polymers such as PE, PS, and PMMA have been studied by using molecular dynamic calculations [46,47], the Monte Carlo method [48,49], and kinetic calculations [50–53]. These studies are able to describe the thermal degradation behavior of polymer chains in a polymer sample and the resulting degradation products, but they are based on imposed spatially uniform temperatures, and no transport processes are included (Some of these calculations were similar to thermogravimetric experiments, i.e., linear temperature increase with time.) Although mass transport of degradation products has been included for wood [54,55] and bubble growth for coal [56,57], these processes are hardly included or even considered for the gasification of synthetic polymers except for Wichman's work [58] on steady-state gasification of PMMA under a specified external flux. A model describing the time-dependent gasification rate of PMMA has been described using a one-step global in-depth degradation reaction (no discussion was given for the kinetic constants used) with heat conduction and with no mass transport process; the numerically calculated results show reasonable agreement with the experimentally measured gasification rates under various external radiant fluxes [34]. Recently, a simple model based on four different chemical reactions, one in the condensed phase and three in the gas phase, was published; but it appears that this model is rather limited because no transport processes are included in either the condensed phase or the gas phase [59].

There are numerous models based on the partial differential equations for conservation of mass, momentum, energy, and chemical species applied to specific aspects of combustion of synthetic polymers such as ignition, flame spread, and extinction. Reviewing these papers is beyond the scope of this paper; excellent review articles are already available [60–63]. However, almost all these models are based simply on condensed phase heat conduction with a one-step global degradation reaction at the surface of the polymer sample or distributed in the sample without any mass transport in the sample. Generally, the gas phase phenomena are treated in much more detail. One of the models is extended to include a detailed description of radiative heat transfer from the flame to the sample surface [64]. It is clear at present that the models for the gas phase are more advanced and include many important physical pro-

cesses, reflecting a greater understanding of the gas phase phenomena compared with those in the condensed phase.

The most commonly used approach in fire research (for example, Ref. 67) is the use of Spalding's transfer number concept (B number) or the global heat of vaporization concept [65,66], which aims to simplify still further the condensed phase treatment. This approach (sometimes called a thermal model) requires only a few quantities describing the condensed phase: the pyrolysis surface temperature, heat of vaporization, and specific heat of the material. (Basically, it is assumed that the heat transfer characteristic time in the condensed phase is much longer than the degradation reaction time and characteristic time of mass transport through the sample.) Although this approach is very convenient for the relative determination of material combustibility and is often used for engineering analysis of fire growth modeling, this can only apply strictly for the steady-state-burning case [22], and further refinement is needed to extend its application for more common time-dependent cases and also for char-forming materials [68]. This concept has been further extended to charring materials, assuming a constant char-forming degradation temperature and heat of formation of the char. Once the char is formed, it is assumed to be inert, acting only as an insulation layer [69]. A more global approach has been used to express the transient gasification rate of PMMA and particle board, heated by external radiation, as a function of the transient total amount of energy stored in the sample [30–32]. This was demonstrated for the case of a constant external radiant flux [31] and also the case of a variable external radiant flux in a nitrogen atmosphere [30]. Agreement between the model and experimental results for the effect of surrounding oxygen on particle board and the effect of the sample thickness [32] are not as good as in the case for PMMA.

Measurement of Flammability Properties and Their Use

As described above, the theoretical models are not advanced enough to predict flammability characteristics of new polymers. Furthermore, since there is an endless number of polymer products having different molecular weight and additives (often not described in the final products), it is impossible to measure all necessary material characteristics for each of these products in an attempt to predict their flammability characteristics. For this reason, flammability characteristics of commercially available polymer products, including the experimental polymers, are measured by various bench scale test methods (The main reason to measure flammability characteristics is that these materials must meet required fire per-

formance levels, as described in the Introduction.) Such tests do pick up significant effects of compositional changes on flammability, but they cannot be used to predict what these effects may be.

Test Methods:

There are many different tests for assessing the flammability of materials. In general, all of the traditional tests express their results in terms of certain observations or measurements. These are then used to derive a relative ranking scale or index on which to evaluate materials. Unfortunately, the bases of these ranking scales are arbitrary, and therefore, results from one test do not necessarily agree with another [70], nor do they reflect how a material might behave in a real fire.¹ However, more recent test methods tend to measure various flammability properties of materials under well-defined conditions that usually include an external radiant flux, and the results are used as inputs to fire growth models or the results are analyzed using theories of combustion to derive values of critical parameters that determine flammability properties [71]. Here, a brief description is given only of flammability test methods that are commonly used in studies to understand the effects of the polymer chemical structure on flammability. More detailed discussion of many tests can be found, for example, in Refs. 72 and 73.

The oxygen index test (ASTM D 2863, often referred to as the LOI test) measures the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that just supports flaming combustion of a sample that burns downward in a candlelike configuration (width 6.5 mm \times length 70–150 mm \times thickness 3 mm). Problems caused by melting and the results depending on the sample thickness and geometrical configuration were reported for this test [74]. The relevance of this test to real fires has been questioned (the test measures the trend of an extinction limit of a material only under the specific conditions tested), but many chemists have long been using this test since the required equipment is inexpensive and only a small sample size is required.

More modern tests that can measure the flammability characteristics of ignition, heat release rate, and combustion products are the Cone Calorimeter Test (ASTM E 1354) [75] and Factory Mutual Research Corporation's Flammability Apparatus [66]. These tests determine transient heat release rate by measuring transient oxygen consumption rate in the exhaust gases. Since the heat release from the unit mass of oxygen consumed during combustion is

nearly a constant (13.4 MJ/kg) for all organic materials [76], the transient heat release rate can be calculated as the product of this constant and the mass consumption rate of oxygen. The development of oxygen consumption calorimetry has made a significant impact on the advancement of fire research, not only because heat release rate is one of the key parameters determining fire characteristics but also because this technique allows measurement of the transient heat release rate of large objects such as furnishings burning by themselves or in a room [77]. This information can be used to predict the gas flow motion induced by the fire and also the transport of combustion products in a building [78].

Another modern test is the LIFT (Lateral Ignition and Flamespread Test, ASTM 1321) [79]. This test is designed to measure lateral (opposed flow) flame spread rates over the range of fluxes or surface preheat temperatures typical of fire. The size of the LIFT flame spread sample is about 15 \times 80 cm. The external flux from a gas-fired radiant panel varies from a high value at the end closest to the panel to a low value (a few percent of the high value) at the other end furthest from the panel (the panel is placed at an angle relative to the sample surface instead of parallel to it). Piloted ignition is performed at the high flux end, and arrival times at fixed locations of the traveling flame front along the sample surface from the high flux end to the low flux end are measured. A flammability diagram consisting of ignition delay time and flame spread rate vs external flux can be derived. Three important material characteristics are derived from this test: inferred gasification surface temperature, the product of thermal conductivity, density, and specific heat of the material, $k\rho c$, and energy feedback function from the flame front to the sample surface [79]. These parameters and the models of which they form elements can be used to describe the behavior of the material in the context of a compartment fire.

Upward Flame Spread on a Wall:

Flame spread up a vertical wall is a component of many fire scenarios; it is important to be able to predict whether a flame will spread up the wall or not (and, if so, how fast) when a small ignition source is located at the bottom of the wall. If the flame spreads partially, how far up will it go? There are several relatively simple models to answer such questions using material parameters inferred from the Cone Calorimeter and LIFT or equivalent tests [80–83]. Slightly more detailed models are also available [84,85][†] but the most simplified model [83] is used

¹One of such tests is the UL-94 test, which is commonly used in industry. However, the test is only relevant to the fire scenario in which a small sample is ignited by a small external fire source such as a flame.

[†]There are more detailed models of flame spread, but they are beyond the scope of this paper; generally, however, the increased detail is in the gas phase instead of in the condensed phase. They can be seen in the recent review article [62].

here to demonstrate how the flammability properties measured in the above tests can be used to predict upward flame spread phenomena. The advantages of this most simplified model are that an analytical solution can be derived and the physical factors influencing upward flame spread can be clearly identified. In this model, the movement of the pyrolysis front measured relative to the bottom of the wall, y_p , is expressed as [83]

$$\frac{y_p}{y_0} = \frac{(a + 1)}{a} e^{at} - \frac{1}{a} \quad (1)$$

where $a = k_t \dot{Q}_{\text{avg}}'' - 1$, y_0 is the initial pyrolysis length due to the ignition source, and $y_0 = k_t \dot{Q}_0''$. The parameter k_t is a constant in the relation between flame tip height and total heat release rate per unit width [86], and \dot{Q}_{avg}'' is the average heat release rate per unit area of the pyrolyzing material, \dot{Q}_0'' is the heat release rate of the ignitor per unit width, and $\tau \equiv t/t_{\text{ig}}$, where t_{ig} is ignition delay time of the material at the average flame heat flux. The parameter a must be greater than zero in order for the upward flame spread process to accelerate, as shown in Eq. (1). The values of \dot{Q}_{avg}'' and t_{ig} are measured in the above tests.⁵ The calculated results show a reasonable agreement with the experimental data in Ref. 83. However, some uncertainty in the measurement procedure for the flammability properties of polymer materials that intumesce during burning was raised [87]. Similar concern was raised for composite materials due to the delamination of the materials and the preferential transport of degradation products through the composite materials, although the comparison of the calculated flame spread behavior agrees reasonably well with the experimental data for a large-size composite panel [88]. This type of approach using a fire growth model in combination with flammability properties measured by well-defined tests as inputs to the model is more scientifically sound for assessing material behavior in fire than the previous ad-hoc-type screen tests. Thus, further refinement of models and analysis of flammability properties are in progress [89].

Effects of Polymer Structure on Flammability

Although values for flammability properties of many synthetic polymers can be found in the published literature, some caution is needed in inferring the effects of polymer structure on this flammability. The same generic name applied to two commercial polymers [90] does not necessarily mean they have

the same molecular structure, and there might also be significant differences in additives, molecular weight, branching, copolymers, and so on. Furthermore, sample size, particularly thickness, must be kept the same between the samples if flammability results are to be compared. Although a conventional approach provided useful global trends of materials composition on flammability properties [91], the results obtained from this type of study cannot clearly show what chemical and physical characteristics are most important for flammability behavior. One approach, which chemists use often, is the pyrolysis study, generally a thermogravimetric study [92] or differential scanning calorimetry [93], to elucidate flammability performance of polymers. Van Krevelen [19] combined a thermogravimetric study to determine char residue in wt% at 850 °C with limiting oxygen index data and derived a simple empirical correlation.

Other empirical correlations have been derived between LOI and the heat of combustion of polymers instead of with char yield [94,95]. Although there is some question about the applicability of the LOI data to actual fire performance, as described above, it has been demonstrated that higher char yield polymers have lowered gasification rate [96], and also that physical char structure has significant effects on flammability properties [97,98]. As a latter example, the addition of a small amount of polydimethylsiloxane into polycarbonate does not significantly change char yield but generates a foamy better-insulating char that reduces the peak heat release rate significantly [98].

Since the viscosity of a molten polymer depends strongly on molecular weight [99], the initial molecular weight of a polymer sample might have significant effects on the transport of the degradation products generated by in-depth thermal degradation reactions to the burning surface. In order to determine the effects of molecular weight and thermal stability of polymers on flammability, materials must have almost the same thermal properties to assure their having the same heat transfer characteristics and also almost the same degradation products to insure that the same gas phase reaction characteristics occur. In a study of these issues, two types of polymers, PMMA and PS, were selected because the thermal degradation of PMMA is controlled by weak linkages in the polymer chains [100,101], and the thermal degradation of PS is controlled mainly via intermolecular- and intramolecular-transfer reactions, not by weak linkages [102,103]. Thus, it is expected that the thermal stability of PMMA is sensitive to initial molecular weight because of a change in the number of weak linkages, but the thermal stability of PS is not sensitive to initial molecular weight. Two PS samples with two different initial molecular weights should indicate only the effects of melting characteristics of the sample on flammability.

⁵There is some uncertainty in the concept of this model regarding under what external flux these values should be measured.

ity. Two PMMA samples with two different initial molecular weights should indicate the combined effects of melting characteristics and thermal stability of the sample on flammability. Using these four different samples, the effects of melt viscosity and thermal stability on piloted ignition [104], flame spread [22], and burning rate [36] were examined. The results indicate that the transport of in-depth degradation products of PS and PMMA through the molten polymer layer inside the sample has a negligible effect on both piloted ignition and burning rate at an external flux of 40 kW/m^2 . However, the thermal stability of PMMA has a significant effect on both its ignition delay time (more stable, longer ignition delay time) and its surface temperature at ignition (ignition temperature increased from a range of 260°C – 270°C to a range of 320°C – 340°C for the two types of PMMA samples used in Ref. 104) and also on burning rate at an external flux of 40 kW/m^2 [36]. The ignition data are shown in Fig. 4. The initial molecular weight of the samples (both PS and PMMA) has a significant effect on horizontal flame spreading behavior and its rate. The samples with a high initial molecular weight form a thin molten polymer layer near the flame front, and that layer does not significantly affect flame spread. However, the samples with low initial molecular weight form a substantial molten polymer layer that exhibits an opposed, slow flow fluid motion along the *inclined* vaporizing surface against the traveling flame. This phenomenon significantly affects horizontal flame spreading behavior, forming a wall-like step ahead of the flame front and reducing its spread rate [22]. Downward flame spread over the high molecular weight PMMA sample did not show any dripping, and the flame spread steadily. However, the flame spread over the high molecular weight PS sample spread with a much-enhanced rate compared with the rate for horizontal flame spread, as a result of streaking of small molten polymer balls. The flame over the low molecular weight PS and PMMA samples was self-extinguished during downward flame spreading because of heat loss from streaking downward of small burning polymer molten balls to the cold sample surface [22]. Clearly, if the burning sample surface is vertical, the effects of polymer melt viscosity are potentially much greater.

These results indicate that, in certain experimental configurations, the melting of thermoplastics has significant effects on their flammability properties [22,90,105]. However, this phenomenon has been ignored or avoided by using nonmelting or nonflowing polymer samples, with the result that there is little quantitative (or even qualitative) understanding of how melting affects flammability. Since almost all thermoplastics soften above their glass transition temperature, some will exhibit flow motions in the polymer melt. Another interesting recent observation (although this is a sample thickness effect in-

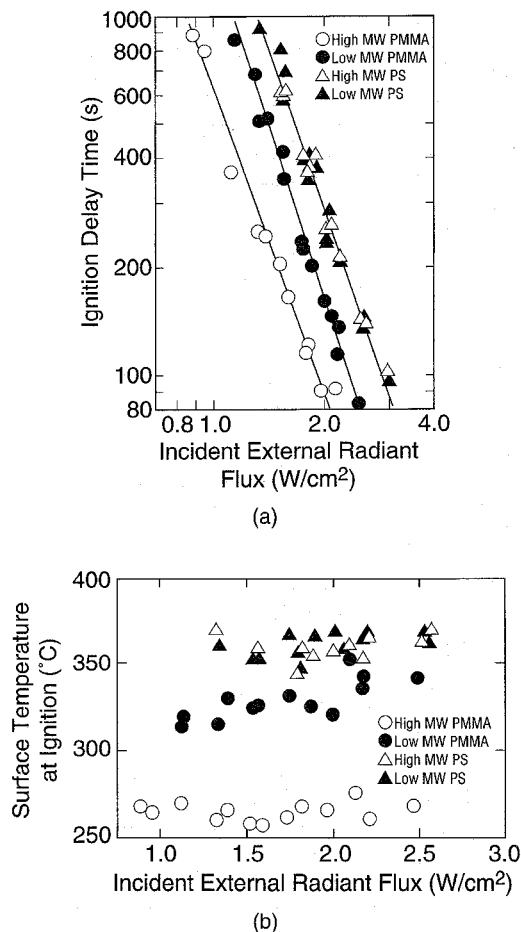


FIG. 4. (a) The relationship between piloted ignition delay time and incident external flux. (b) The relationship between surface temperature at ignition and incident external radiant flux (Ref. 104).

stead of polymer structure) is that a thermally thin material burning on both sides will do so at a rate significantly more than twice the value seen when only one side is burning [106]. Two simplified models demonstrate that this is a consequence of the Arrhenius temperature dependence of the gasification rate of the solid.

With the advancement of the polymer synthesis field, many new inorganic polymers have been formulated. Their backbone elements are mainly silicon, nitrogen, and phosphorus rather than the carbon of organic polymers. Their combustion behavior could be significantly different from that of the carbon-based polymers. One such example is the combustion of polydimethylsiloxanes, PDMS. PDMS samples having low initial molecular weights burn similarly to hydrocarbons except for the formation of silica particles in the flame [107]. However, PDMS

samples having a high initial molecular weight form a layer at/near the surface consisting mainly of silica (35–45% of original Si), and this layer becomes thicker and has greater mechanical integrity as molecular weight increases. Energy feedback from the flame is inhibited sufficiently by this layer to cause self-extinguishment [108] or to yield a near-constant burning rate even with an increase in external flux [109]. The accumulation of silica at/near the surface of the PDMS samples could be caused either by thermal degradation in the condensed phase or by downward transport (convection/falling/thermophoresis) of silicate particles formed in the flame.

Flame Retardants

The fire safety of materials can be enhanced by increased ignition resistance, reduced flame spread rates, lesser heat release rates, and reduced amounts of toxic and smoke products, preferably simultaneously. The use of more thermally stable polymers, of which many are available, might be a valid solution to these requirements, but generally, the cost of these materials is relatively high, and furthermore, their physical properties or processability may not be as desirable as those of less stable polymers. The most common approach to enhance fire safety performance is the use of flame-retardant additives to inexpensive polymers (large volume commodity polymers such as PE, PP, PS, PVC, and so on). The additives must have a minimum impact on physical properties and product cost. Although halogenated flame retardants are highly effective for reducing the heat release rate of commodity polymers, the future use of these retardants faces some questions. The environmental impact of the processing and combustion of certain halogenated flame retardants has become an issue in Europe. Laboratory and field studies indicate that one class of brominated flame retardants, the brominated diphenyloxides, may serve as precursors for the formation of potentially hazardous polybrominated dibenzo-*p*-dioxins and polybrominated dibenzofurans in yields of up to 16% [110,111]. Furthermore, there is some concern regarding the potential production of bromodioxins and furans from combustion of waste plastics containing such brominated flame retardants during incineration. The environmental effects of the widespread use of chlorinated compounds was debated in a recent publication [112], and concern over the possible corrosion damage to metals by the combustion products from fire in which plastics containing halogenated additives or groups are involved may impact the use of halogenated compounds. As our society becomes more dependent on high technology, the corrosion threat from fire in communication and electronic systems could become a major problem. Because of an increase in public awareness of the

potential environmental effects of halogenated compounds and an increase in worldwide legislation on corrosivity of fire products, studies aimed at developing other types of flame-retardant treatments are on-going.

Although there are many possible approaches to nonhalogenated flame retardancy, such as the use of aluminum trihydrate or magnesium hydroxide (both generate water and act as a heat sink), intumescent coatings, and so on [113,114], an interesting and promising approach is the formation of char; only the current status of this latter approach is discussed in this paper. There are three mechanisms whereby the formation of char reduces flammability: (1) part of the carbon (and hydrogen) stays in the condensed phase, thus reducing the amount of gaseous combustible degradation products evolved; (2) the low thermal conductivity of the char layer over the exposed surface acts as thermal insulation to protect the virgin polymer beneath [115]; and (3) a dense char acts as a physical barrier to gaseous combustible degradation products [116]. As described in Ref. 19, some polymers form char when degraded in a fire, but others do not. In order to understand how to form char or increase its amount, it is important to study the chemical and physical structure of char.[#] Reference 18 presents excellent work on detailed analysis of the residues formed from aromatic engineering polymers to determine their chemical structure. Elemental analysis of the chars formed from bisphenol A polycarbonate, BPA-PC, indicates that an increase in pyrolysis temperature increases C/H ratio from an initial value of 1.14 to 1.87 at 591 °C. The Raman spectra and the photoacoustic Fourier transform infrared (FTIR) spectra of the chars show the presence of small graphitic regions in the chars. The infrared spectra of the BPA-PC chars (Fig. 5) show progressive changes in the material, revealing loss of the carbonate group (1775 cm⁻¹) and aliphatic C-H groups (2982 and 1385 cm⁻¹), and the growth or appearance of hydroxyl groups (3580 cm⁻¹), aromatic C-H groups (3012 and 3058 cm⁻¹), ester groups (1740 cm⁻¹), ether groups (1170 and 1260 cm⁻¹), and new aromatic groups (1900, 1610, 752, 820, and 880 cm⁻¹). These results and the solid state ¹³C NMR results indicate that, when BPA-PC and other aromatic polymers are heated, they lose most of their aliphatic groups, resulting in predominantly protonated and unprotonated aromatic carbons in the residual char. It should be noted that char has no unique structure but rather reflects the starting polymer and its heating rate history.

As noted in the previous section, the physical structure of char has significant effects on polymer

[#]There are numerous publications on the formation and characterization of carbon. Although these publications are relevant to char, this subject is beyond the scope of this paper.

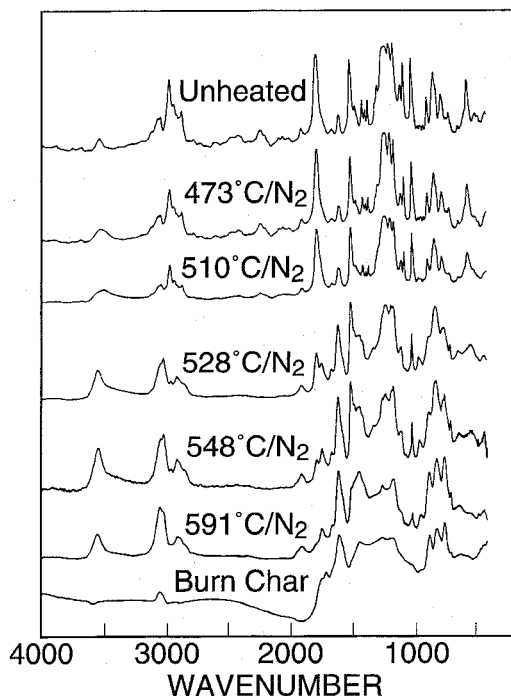


FIG. 5. Photoacoustic FTIR spectra of bisphenol A polycarbonate (Ref. 18).

flammability. It is generally preferable to form an intumescent char (swollen char) having a cellular interior structure consisting of pockets of trapped gas [117]. The dominant protective role of an intumescent char is mainly via its thermal insulating capability [116,117] rather than an obstacle to the passage of volatile and low-viscosity products into the gas phase because low-viscosity polymeric melts can rise through an intumescent char layer as a result of the capillary forces [118].

The majority of commodity polymers do not form char during their combustion, and current research seeks to determine how to form an intumescent char in these polymers. A precise sequence of events is required to form an intumescent char when a polymer is exposed to heat. This is illustrated by the sequence employed in commercial intumescent coating. After the coating sample is sufficiently heated to become softened, a blowing agent must be released. The blowing agent can be released by endothermic decomposition of a hydrated salt that releases water as the blowing agent or the decomposition of an acid salt to yield an anhydrous acid. This anhydrous acid is capable of esterification of polyols. The acid acts as a dehydration agent that, with subsequent heating, leaves a carbonaceous residue. The "timing" (the temperature sequence of each step) is very important [114,117,119,120]. The acid-organic polyol must

melt prior to or during esterification so that when the polyol decomposes via dehydration (forming a carbon-inorganic residue), the released blowing agent and the evolution of other nonflammable gases cause the char mass to intumesce and foam. The insulation efficiency of the char depends on the cell structure formed. The structure in turn depends on the staging of the blowing agent relative to the formation of a critical viscosity in the semimolten layers. If the blowing agent action occurs too early, the intumescent action is reduced because the molten material is too viscous. If the action occurs too late, solidification of the char inhibits intumescence. If the molten material becomes too fluid (the viscosity becomes very low), large cells are formed during the blowing process and in the char. These large cells are relatively ineffective as insulators, and the char can become quite fragile. Thus, if any one of the steps does not proceed at the required time, intumescence does not occur or is severely limited. Although a large effort is being carried out by industry to develop new, more highly effective systems, more systematic studies are needed to understand chemical and physical mechanisms of this complex intumescent char-forming process. In order to complement this effort, development of theoretical models to describe the intumescence process is also needed. Previously published models of intumescent char formation [121,122] are rather limited, and further progress is critically needed.

Conclusions and Future Needs

The above discussion clearly shows that fundamental understanding of chemical and physical mechanisms in the condensed phase during combustion of polymers is severely lacking compared with that in the gas phase. Although the overall thermal degradation mechanisms of vinyl polymers are relatively well known compared with those for engineering polymers, available models do not have the capability to predict the evolved rate of degradation products from these polymers except in a few limited cases that exclude any transport processes. Some of the difficulties are a lack of kinetic constants for specific degradation reactions such as intermolecular transfer reactions, which are often not only a function of temperature but also the mobility of polymer chains and the degree of tangling of polymer chains (cage effects). Furthermore, if these kinetic constants are available, generally they are measured at much lower heating rates than those encountered in fire. It is still debatable whether application of kinetic data from low heating rate experiments to high heating rate fire processes is appropriate or not.

The heat and transport processes in the polymers must be better understood, particularly the latter. The roles of bubbles and of oxygen in the gasification

process must be clearly understood. If the gasification is significantly affected by bubbles, the transport mechanism of bubbles through the molten polymer layer to the sample surface must be understood. Another important transport process is polymer melt flow. Using the information available in the field of polymer processing (injection molding), it might be feasible to characterize the polymer melt flow given the distributions of temperature and molecular weight.

Elucidation of char-forming chemical mechanisms and of the chemical and physical structures of chars is needed to permit the enhancement of the formation of char. The thermal properties of char, the heating effects on char yields, and porosity of char must be studied to find the optimum char structure for maximum reduction in flammability.

Acknowledgments

The author is grateful to Dr. Richard G. Gann and Professor Toshisuke Hirano for the invitation to present this paper; to Professors Dougal Drysdale and Giovanni Camino and Dr. Arnold Factor for providing copies of their papers; to Professor A. Carlos Fernandez-Pello for providing his review article (in print); to Dr. Thomas J. Ohlemiller for an extensive, constructively critical review of the manuscript.

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COMMENTS

R. H. Essenhigh, *Ohio State University, USA*. 1. Can you comment on the fragment size of the decomposed polymers, either from measurements or from modeling. Did the polymers degrade to monomer (or were they assumed to do so) and/or did the monomers themselves also degrade? The background to my question is work we reported

in 1969 and 1973 [Essenhigh and Dreier, *Fuel* 48:330 (1969) and Waibel and Essenhigh, *International Symposium on Combustion*, 1973, p. 1413] on combustion of a range of thermoplastic polymers. We concluded from analysis of data on flame standoff distance and particle/droplet temperatures that the evaporating fragment was generally

2–10 monomer units in size; the polymers did not degrade to monomer. One associated consequence was that the large molecular weight resulted in smaller diffusion coefficients compared with oils, resulting in smaller flame standoff distances, and hence with steeper temperature gradients the evaporation and thus the burning rates were correspondingly increased. The measured burning rates were roughly three times faster than light oil drops. Is this factor likely to be relevant in your studies?

2. With reference to the thermoplastic nature of the polymers with viscosity, a definable function of temperature, you may know that this is also true for coals. Comparisons with coals might be informative.

Author's Reply. 1. Only a few polymers, such as polymethylmethacrylate (PMMA), poly α -methylstyrene, and polytetrafluoroethylene, generate monomers as the main degradation products. It appears that the effects of higher heating rate on PMMA degradation products are negligible. [Seshadri, K., and Williams, F. A., *J. Polymer Sci. Polymer Chemist Ed.* 16:1755–1778 (1978).] All polymers used in the paper you cited, except PMMA, generate many different sizes of fragments. The pyrolysis occurs at the surface or in depth depending on the heating rate and the thermal stability of the polymers. After reading the two papers you cited, it appears that degradation reactions occurred over some depth in the samples but not necessarily over the entire volume. The competition between polymerization and depolymerization is determined by the ceiling temperature of a polymer. If the polymer temperature is higher than its ceiling temperature, depolymerization exceeds polymerization. This temperature depends on the type of polymer; for PMMA it is 197 °C, and for styrene it is 384 °C [16]. Since the measured polymer temperatures are much higher than these values, the polymerization suggested in the paper appears to be negligible and large fragments are generated directly by degradation reactions. The physical and chemical processes observed in the burning of plastic spheres cited in the two papers by Professor Essenhigh are directly relevant to our studies.

2. The melt viscosity of polymers is well studied and quite definable. A good reference is Brydon, J. A., *Flow Properties of Polymer Melts*, George Godwin Limited, London, 1981. Many different approaches and techniques taken in coal research are quite useful to pursue for polymer combustion research. However, since chemical and physical structures of polymers are much more clearly defined than those of coals, quantitative information about coal might not be as useful as qualitative information.

D. Milov, RRA, USA. This was an excellent presentation and review. The author, however, completely ignored an issue: radiation from the flames of pyrolysing gases. This radiation drives the fire growth process. Does the author agree that some (or a lot of) effort should be directed toward formulating new materials that (1) produce char (as the author also proposes) and also (2) reduce (soot) radi-

ation? So, maybe oxygen- or nitrogen-containing materials can be developed that when pyrolysing produce reduced soot amounts (because of oxidation or inerting). The same materials must also have charring or intumescent behavior.

Author's Reply. Although a reduction in the radiative feedback rate from the flame to the fuel surface could be considered as one way to reduce the burning rate of polymers, generally a reduction of soot is more frequently sought due to the need for meeting soot-related regulations. These regulations are set to increase visibility and thus make evacuation from a fire scene easier. Char formation tends to reduce the amount of evolved combustible gases which, in turn, reduces flame height and also radiative feedback rate (shorter radiative path). An increase in the amount of char often requires incorporation of aromatic rings into the polymer chain, which might increase the soot yield. Therefore, the location of these rings in the polymer chain becomes very important to avoid the generation of soot while enhancing the formation of char (Polystyrene does not generate any char, but poly *p*-phenylene generates a lot of char.)

Yes, the addition of oxygen and nitrogen into a polymer chain tends to reduce the generation of soot. The former also reduces the heat of combustion, but the latter might generate HCN.

Richard G. Gann, NIST, USA. In this talk, you have shown that improved fire performance can be achieved by chemical changes in the material, changes that have little effect on the material's physical properties. Conventional models of burning and flame spread center on thermo-physical properties (e.g., k , ρ , c). What, then, are the implications of these findings for flammability modeling?

Author's Reply. Since there are an endless number of polymer products having different molecular weights and additives (often not described in the commercial products), it is essentially impossible to measure all necessary physical and chemical characteristics for each of these products in an attempt to predict flammability characteristics. Therefore, chemical effects are globally included through the values of gasification (pyrolysis) temperature, ignition temperature, or global heat of vaporization. However, if we want to improve the flammability of a specific polymer or develop a new approach to flame retardancy, we need to model in detail the physical and chemical processes in the condensed phase using the well-defined polymer. Such detailed models serve a research role distinct from more empirical models that attempt to relate small-scale test behavior to full-scale fire performance.

A. M. Kanury, Oregon State University, USA. You described clearly the very interesting and important feature that low molecular weight polymers tend to melt more easily and flow ahead of a downward propagating flame and

that such a melt flow can even produce flame quenching. Can you comment on whether this reduction in burning to quenching can be modelled by viewing the drip process as either reducing the effective heat of combustion or increasing the effective latent heat (L_{global}) of phase change?

Author's Reply. Although it could be possible to model these phenomena as you suggested, I would like to see models that describe the observed physical phenomena correctly. Since research on polymer processing such as injection molding and compounding is quite active and has provided much relevant information, it is quite feasible to model polymer melting flow phenomena explicitly.

Andreas Hornung, Universit t Kaiserslautern, Germany. How did you calculate the high activation energy of about 700 kJ/mol for the decomposition of C-C double bond systems like polyacetylene and in which temperature range does the decomposition takes place?

Author's Reply. The slide that shows the relationship between bond dissociation energy and external radiant flux was provided by Dr. Richard Lyon at the Technical Center of Federal Aviation Agency, Atlantic City, NJ, and he used the data from *CRC Handbook of Chemistry and Physics*, 63rd ed., The Chemical Rubber Co., Cleveland, 1982/83, p. F-198.